

Peculiarities of anharmonic effects in the lattice thermodynamics of fcc metals

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Abstract

Explicit expressions for anharmonic contributions to the thermodynamic properties with allowance for higher-order phonon-phonon interactions for closed-packed crystals are given, and the calculations for some fcc metals near the melting (Ir, Rh) and martensite phase transition (Ca, Sr) points are carried out. A detailed comparison of anharmonic and electron contributions to the heat capacity of these metals is carried out. The computational results for high-temperature heat capacity agree well with the available experimental data.

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Anharmonic effects (AE) in the lattice dynamics and thermodynamics have been extensively discussed in the literature [1-5]. However the quantitative information on AE, both experimental and theoretical, is rather poor so far. The experimental difficulties are due to the fact that at high temperatures ($T \sim T_m$, where T_m is the melting temperature) when the AE in the thermodynamic properties become noticeable, it is usually difficult to identify their contribution to the heat capacity and thermal expansion from the contributions of vacancies and other thermally excited lattice defects [2,5-8]. The theoretical calculations, on the other hand, are based, as a rule, on rough models and, therefore, do not give any definite information on the AE in thermodynamic of real crystals. At the same time this information is needed for understanding the high temperature properties of solids. For example, it is important to clear up what is the role of self-anharmonic effects associated with phonon-phonon interactions, and what is the role of quasiharmonic ones which are only due to the change in the volume because of thermal expansion. Simple estimations [9] show that the AE contribution to heat capacity at high temperatures of the order of the electron contribution to heat capacity and has the same (linear) temperature dependence; the real ratio of these two contributions essentially depend on the features of the electron structure near the Fermi level E_F . However this problem has not been studied yet. All these problems are of special importance for refractory metals ($T_m > 2000$ K) and for the metals with high-temperature martensite transitions which

are usually accompanied by essential increase in the AE in the lattice dynamics [10]. In the present work the AE features (in the comparison with the electron contributions) in the thermodynamical properties of refractory fcc metals Ir and Rh and in the bcc and fcc phases of Ca and Sr near the points of structural transformation are studied. The calculations were made in terms of microscopic models used in [10, 11] which describe a wide range of the lattice properties of these metals.

The initial Hamiltonian of phonon subsystem is

$$H = \sum_{\lambda} \left(\frac{P_{\lambda}^2}{2M} + \frac{M\omega_{\lambda}^2 Q_{\lambda}^2}{2} \right) + \sum_{n=3}^{\infty} H^{(n)} \quad (1)$$

$$H^{(n)} = \sum_{\lambda_1 \dots \lambda_n} \frac{\Phi^{(n)}(\lambda_1, \dots, \lambda_n)}{n!} Q_{\lambda_1} \dots Q_{\lambda_n} \quad (2)$$

where M is the mass of atoms; ω_{λ} is the phonon frequency, $\lambda \equiv \mathbf{q}\xi$ where \mathbf{q} – is the wave vector; ξ is the branch number, Q_{λ} , P_{λ} are the normal coordinates in the harmonic approximation and the corresponding pulses, $\Phi^{(n)}$ are amplitudes of intermode interactions. In the leading order of the parameter $\eta \equiv T/E_{at}$ where E_{at} is the energy of the order of binding energy, the basic contribution of AE to free energy F is determined by the second order by $H^{(3)}$ and the first order by $H^{(4)}$ [1, 2]

$$F_{an} = F^{(3)} + F^{(4)} \quad (3)$$

where at $T \gg \Theta_D$ (Θ_D is the Debye temperature),

$$F^{(3)} = -\frac{T^2}{12M^3} \sum_{\lambda\mu\nu} \frac{|\Phi^{(3)}(\lambda, \mu, \nu)|^2}{\omega_{\lambda}^2 \omega_{\mu}^2 \omega_{\nu}^2}, \quad (4)$$

$$F^{(4)} = \frac{T^2}{4M^2} \sum_{\lambda\mu} \frac{\Phi^{(4)}(\lambda, \lambda, \mu, \mu)}{\omega_{\lambda}^2 \omega_{\mu}^2}; \quad (5)$$

as usually, summing over phonon quasimomenta is fulfilled taking into account the conservation law for $\lambda \equiv (\xi, \mathbf{k})$, $\mu \equiv (\eta, \mathbf{q})$, $\nu \equiv (\zeta, \mathbf{k} + \mathbf{q})$. The explicit microscopic expressions for $\Phi^{(3)}$ and $\Phi^{(4)}$ are given in [2].

The heat capacity of the crystal at $T \gg \Theta_D$, without the standard harmonic contribution $C_V^{harm} = 3R$ (where R is the gaseous constant), has the form:

$$\Delta C = C_P - C_V^{harm} = (C_P - C_V) + C_V^{an} + C_V^e + C_V^d \quad (6)$$

where C_V^{an} are the anharmonic contributions to the heat capacity

$$C_V^e(T) = \frac{R}{T} \int_{-\infty}^{\infty} dE \left[-\frac{\partial f(E)}{\partial E} \right] (E - \mu)^2 N(E) \quad (7)$$

is the electron heat capacity ($N(E)$ is the electron density of states, μ is the chemical potential, $f(E)$ is the Fermi distribution function), C_V^d is the contribution of defects;

the calculation formula for $C_P - C_V$ in the quasiharmonic approximation is presented in [2]. The density of states $N(E)$ was calculated by the FP-LMTO method in the local approximation for the density functional (LDA) [12]. To estimate the contribution of defects to the heat capacity a common approximation of independent monovacancies was used with

$$C_V^d(T) = R \left(\frac{E_v}{T} \right)^2 \exp \left(S_v - \frac{E_v}{T} \right) \quad (8)$$

where E_v , S_v are the energy and entropy of monovacancy formation, respectively.

The calculations of AE in the Ir lattice dynamics, made in [11], show that near the melting temperature $T = T_m$ the temperature dependences of the phonon frequency and phonon damping drastically change over the Brillouin zone reaching the values of the order of 15-20%. This value is high enough so that the question on the role of higher orders in the anharmonic perturbation theory could be set. The theory of self-consistent phonons, often used for this purpose (see, e.g., [13]) is not adequate in this case as it only accounts for a part of $H^{(2n)}$ contributions to (1) and neglects the $H^{(2n+1)}$ contributions. At the same time, the calculations [11] show that in Ir the contributions of three-phonon processes to the temperature shifts of the phonon frequencies always dominate over the contribution of four-phonon processes. In the recent work [4] another approximation is proposed which accounts both the three-phonon and four-phonon processes, and, as stated, reasonably describes the thermodynamics of crystals with the Lennard-Jones type interaction. The applicability of this approximation in the case considered seems somewhat doubtful as it is based on the replacement of anharmonic frequency shift by a certain value average over the Brillouin zone while the calculations in [11] show that the \mathbf{q} -dependence of AE is essential. Moreover, it is known that the approximations adequate for the description of thermodynamics of systems with “hard” potentials of Lennard-Jones type are not usually applicable for metals as they have relatively “soft” potentials [2].

To calculate the effects of higher orders by the Hamiltonian $H^{(3)}$ the approximation similar to that of Gell-Mann and Brueckner (“bubble approximation”) in the theory of electron liquid [14] was used. It can be shown that the accurate expression for the contribution of three-phonon processes to the free energy at $T \gg \Theta_D$ has the form:

$$F^{(3)} = -\frac{T}{3} \int_0^1 \frac{d\alpha}{\alpha} \sum_{\lambda} [G_{\lambda}(\omega=0) \Sigma_{\lambda}(\omega=0)] \Big|_{H^{(3)} \rightarrow \alpha H^{(3)}} \quad (9)$$

where G_{λ} , Σ_{λ} are the Green function and self-energy part for phonon (see [1]) connected by the Dyson equation

$$G_{\lambda}^{-1}(\omega) = \frac{\omega^2 - \omega_{\lambda}^2}{2\omega_{\lambda}} - \Sigma_{\lambda}(\omega). \quad (10)$$

The calculations [11] show that the AE in fcc metals have pronounced peaks as functions of \mathbf{q} at points X and L. The largest contribution to the free energy comes from the “bubble” diagrams; this situation is similar to the electron gas of high density with the only difference that in the latter case the “dangerous” region is $\mathbf{q} \approx 0$ [14]. Taking this into account, in (9)-(10) we may restrict ourselves to the expression of the lowest (second)

order of the perturbation theory for Σ_λ . Then we have

$$F^{(3)} = \frac{T}{6} \sum_\lambda \ln \left[1 - \frac{T}{2M^3} \sum_{\mu\nu} \frac{|\Phi^{(3)}(\lambda\mu\nu)|^2}{\omega_\lambda^2 \omega_\mu^2 \omega_\nu^2} \right] \quad (11)$$

Unlike the bcc metals the fcc metals have no soft modes in the phonon spectrum, which makes the four-phonon processes relatively small comparing with the three-phonon ones [10, 11]. Therefore for $F^{(4)}$ it is sufficient to use the simplest corresponding to the Hartry-Fock approximation (the simplest procedure of disengagement in averaging Hamiltonian $H^{(4)}$). Then for $T \gg \Theta_D$ we have

$$F^{(4)} = T \sum_\lambda \left[\ln \left(1 + \frac{\Delta_{4\lambda}}{\omega_\lambda} \right) - \frac{1}{2} \frac{\Delta_{4\lambda}}{\omega_\lambda} \right], \quad (12)$$

where

$$\Delta_{4\lambda} = \frac{T}{4\omega_\lambda} \sum_\mu \frac{\Phi^{(4)}(\lambda, \lambda, \mu, \mu)}{M^2 \omega_\mu^2} \quad (13)$$

is the corresponding correction to the phonon frequency.

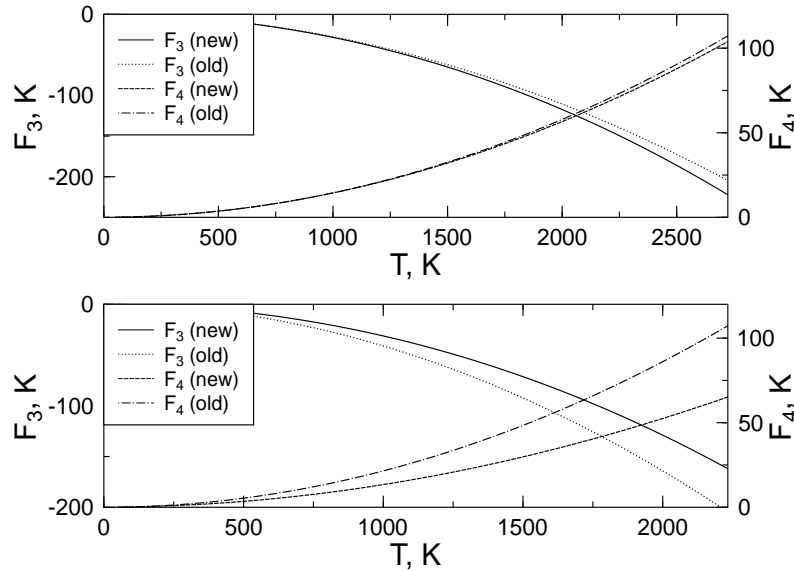


Fig. 1. Anharmonic contributions to the free energy of Ir and Rh (in K) considered by the perturbation theory (4), (5) (“old”) and with taking into account the higher orders (11), (12) (“new”).

The computational results are shown in Figs. 1-5. One can see that the AE higher order contributions to the free energy of Ir and Rh are not large (do not exceed 20%). In Ir and Rh the anharmonic contribution to heat capacity is small comparing with the electron contribution while in the sp-metals (as the hypothetical fcc phase K shown in Fig. 3) these contributions are comparable. Among the metals studied only for Ir the detailed experimental information is available, the theoretical data being in good agreement with these results (Fig. 4). In the estimation of C_V^d according to (8) the the first principles

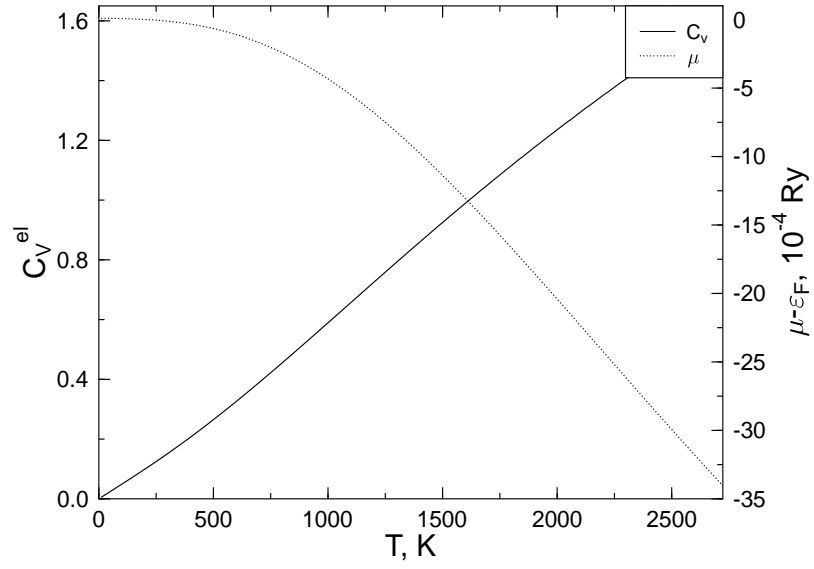


Fig. 2. Electron contribution to the heat capacity (in R units) and temperature dependence of chemical potential (to 10^{-4} Ry) in Ir; the dependencies for Rh are similar.

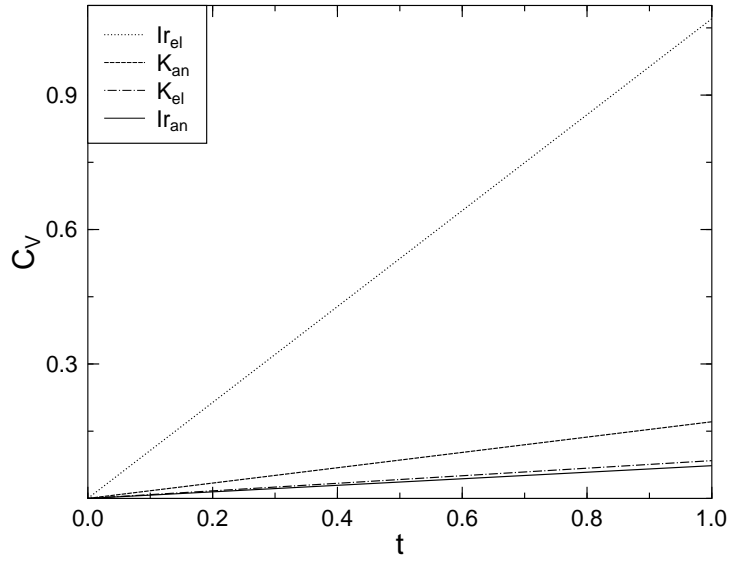


Fig. 3. Comparison of the electron and anharmonic contributions to the heat capacity (in R units) for the fcc phases of K and Ir; $t = T/T_m$.

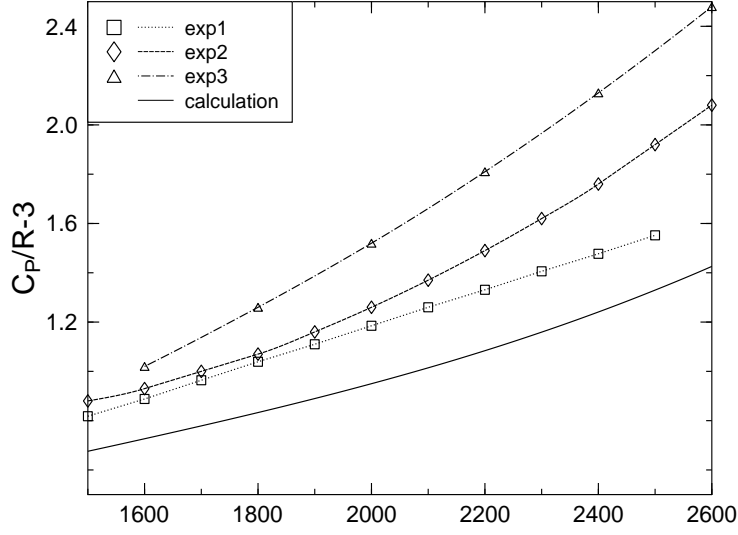


Fig. 4. Comparison of the calculated values of heat capacity C_P (formula (6)) with the experiment for Ir; the data of exp1, exp2, exp3 are taken from [15, 16, 8], respectively.

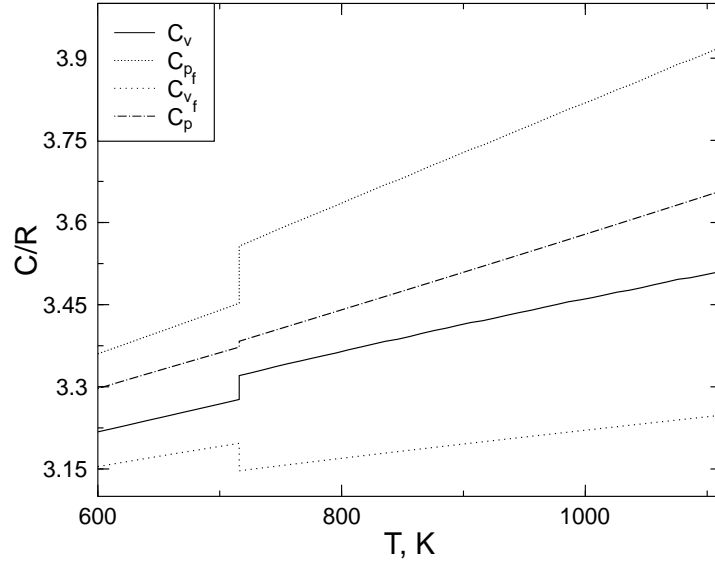


Fig. 5. Theoretical value of heat-capacity in Ca. The notation introduced $C_v = C_v^{harm} + C_v^{an} + C_v^{el}$, $C_p = C_v^{harm} + C_v^{an} + C_v^{el} + (C_p - C_v)$, $C_v^f = C_v^{harm} + C_v^{an} + C_v^{free\ el}$, $C_p^f = C_v^{harm} + C_v^{an} + C_v^{free\ el} + (C_p - C_v)$, $C_v^{free\ el}$ – the electron heat capacity in the approximation of free electrons.

calculation result from $E_v = 1.88$ eV [17] was used for E_v , and $S_v = 2.5$ for S_v [2]. It follows from Fig. 5 that in the difference of heat-capacity for bcc and fcc phases of Ca (and similarly Sr) a strong compensation for different contributions – electron, anharmonic ones – and the contribution of $C_P - C_V$ takes place. Thus, for the discussion of thermodynamics of high temperature structure transformations in metals the microscopic calculations of corresponding values including the anharmonic effects are needed.

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